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Reactions of Silicon Compounds with Organic Hydroxyl Groups

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Thesis

Reactions of Silicon Compounds with Organic Hydroxyl Groups.

by

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Introduction

This thesis is concerned with the reaction of silicon compounds with the replaceable hydrogen of hydroxyl or amino compounds. The reactions of tetraethyl orthosilicate(1) and the partially hydrolyzed ester(2) with the hydroxyl group of polymers have been postulated. Other sources(3)(4) note that halosilanes readily react with organic hydroxyl groups.

It is the purpose of this paper to produce infra-red spectroscopic evidence that the organic hydroxyl group actually participates in the given reaction. Further, it is sought to modify the properties of hydroxyl bearing polymers. Finally, the development of new polymers formed by condensation polymerization of a silicon monomer with a difunctional hydroxyl or amino molecule is initiated.

Part 1. Reactions of Organo-Silicon Compounds with Cellulose

The object of this section is to effect a reaction between the cellulosic hydroxyl and derivatives of tetraethyl orthosilicate or silicon tetrachloride. Infra-red spectroscopy is applied to elucidate the reaction path and to allow an analysis of the extent of said reaction.

Marks(1) and Cogan(5) have indicated there is a direct reaction between tetraethyl orthosilicate and the hydroxyl group of polyvinyl butyral. It is reasonable to consider that the tetraethyl orthosilicate is partially hydrolyzed in the acid medium and that the resulting hydroxyl groups react with the polymer hydroxyl group. It is also possible the tetraethyl orthosilicate may hydrolyze completely forming a polysilicic acid which may be mixed into the polymer without any chemical reactions. In either case, a harder surface would be displayed by the polymer since cross linkage occurs by both the aforementioned processes.

It was thought worthwhile to carry out the reaction between tetraethyl orthosilicate and a polymer to determine if any chemical reaction occurred. It was first necessary to determine the number of hydroxyl groups per glucose unit present in the ethyl cellulose polymer which was used throughout the experiments.

Procedure. Hydroxyl determination by acylation(6)

Dow ethyl cellulose of medium ethoxy content and 10 centipoise viscosity was chosen as the base polymer since it is soluble in a wide variety of solvents. The hydroxyl content was determined by acylation in the procedure described below.

One gram of dried ethocel was weighed into a pressure bottle and exactly 40 cc pyridine-acetic anhydride solution (50 cc acetic anhydride and 950 cc dry pyridine) was added. The bottle was closed and placed in an oil bath at 75-80°C for 24 hours and then removed, cooled to room temperature and 5 cc of water was added. The solution was heated to 80°C for five minutes and then cooled to room temperature and poured into 300 cc of distilled water.

This solution was titrated with 0.5N NaOH to a phenolphthalein end point. Two samples and a blank were run concurrently.

Since the acetic anhydride acylated the residual hydroxyl groups, the volume of standard base used for the blank minus the volume of standard base used for the sample equals the milliequivalents of acetic acid titrated or the milliequivalents of hydroxyl present in the original sample. Multiplying this value times 0.017 gives the grams of hydroxyl in the original sample (A in below formulae).

$$\text{The fraction of hydroxyl by weight} = \frac{A}{\text{Sample weight}} = \frac{(3-DS)\ 17}{159.14+DS(MWS)+(3-DS)}$$

DS = degree of substitution

MWS = molecular weight of substituent = $C_2 H_5$

EWS = equivalent weight of substituent = $C_2 H_5$

SW = sample weight

then fraction of substituent $= \frac{EWS\ (3000\ SW - 162.14(\triangle CC)N)}{1000\ SW\ (162.14 + 3(EWS-1)}$

and degree of substitution $= \frac{3000\ SW - 162.14\ x \triangle CC\ x\ N}{1000\ SW + (MWS-1)\ x \triangle CC\ x\ N}$

Sample a. 1.0278 grams - 74.25CC 0.5N NaOH

b. 1.0808 grams - 74.20CC 0.5N NaOH

Blank ----- - 78.76CC 0.5N NaOH

Sample a. 78.76 − 74.25 = 4.51CC

Sample b. 78.76 − 74.20 = 4.56CC

D.S. sample a. $= \frac{3000 \times 1.0278 - 162.14 \times 4.51 \times 0.5}{1000 \times 1.0278 + (29-1)\ 4.51 \times 0.5} = \frac{2718}{1091}$

$= 2.48$

D.S. sample b. $= \frac{3000 \times 1.0808 - 162.14 \times 4.56 \times 0.5}{1000 \times 1.0808 + (29-1) \times 4.56 \times 0.5} = \frac{2713}{1091}$

$= 2.49$

The average number of hydroxyl groups present is equal to (3-DS) so the ethyl cellulose used in all the following experiments has (3 - 2.48) or 0.52 hydroxyl groups per glucose unit.

Experimental procedures

To the dry toluene solution of ethyl cellulose was added a slight molar excess of the organo-silicon compound. This solution was refluxed to a point just prior to gelation and then several films were deposited on glass treated with Dri-Film. Dri-Film is tri-methylchlorosilane and is simply rubbed on a clean glass surface to present a non-polar surface from which polymer films may be easily removed. Films 0.001" in thickness were obtained and placed in a vacuum oven at 75°C and 4 mm pressure for 72 hours. The film was then transferred to an efficient desiccator and then analyzed.

Films were cast from the following solutions.

mix #1 5 gms. of ethyl cellulose in 100 cc. anhydrous toluene

mix #2 5 gms. of ethyl cellulose in 100 cc. anhydrous toluene and 5 cc. of tetraethyl orthosilicate added

mix #3 5 gms. of ethyl cellulose in 100 cc. wet toluene and 5 cc. of tetraethyl orthosilicate and 0.1 gms. p-toluene sulfonic acid added

mix #4 5 gms. of ethyl cellulose in 100 cc. anhydrous toluene and 5 cc. of partially hydrolyzed tetraethyl orthosilicate added(5)

mix #5 5 gms. of ethyl cellulose in 100 cc. of anhydrous toluene and 3 cc. of silicon tetrachloride added

mix #6 5 gms. of ethyl cellulose in 100 cc. of anhydrous toluene and 3 cc. dimethyldichlorosilane added

Infra-red Spectroscopy

Operation

The above 0.001" films were supported over a one inch hole on an index card and then placed over the transmission window of the Perkin-Elmer spectrophotometer.

In operating the spectrometer for a recorder curve, the micrometer is turned below zero to get the minimum slit width and the gauge locked. The Littrow counter is then turned to 3.6, the recorder drive turned on, the pen moistened and positioned, the motor drive engaged and the curve started at 4 Littrow mirror numbers (L.M.N.) and synchronized to the chart by adjusting the roller knob. It is best to note on the chart the L.M.N. as the energy curve is run. The data are then automatically recorded from 1 to 15 microns, the motor disengaged, the recorder switch turned off, the L.M.N. dial returned to 3.6 and the drum reeled back to the initial position. The sample spectra are then obtained as was the energy curve. The energy L.M.N. data are transferred to percent transmission and microns by dividing the sample energy, at the L.M.N. corresponding to a given wave length, by the energy value and multiplying by 100.

The sample must be about 0.001" thick in order to get a good curve, or else the narrow bands and fine structure

will be lost. It is requisite that the sample be baked in vacuum, as noted above, in order to remove all volatile constituents or products.

Spectrographs

The energy curves (page 9) for the films from mix #1 (ethyl cellulose) and mix #2 (ethyl cellulose and tetraethyl orthosilicate) were obtained. In these, the abscissa is in L.M.N. units and the ordinate in transmitted energy. The data (pages 10 to 17) of the conversion of this curve to a wave length (microns) and percent transmission spectrograph (page 18) are attached. The latter curve is obtained from the energy curve of the recorder by expressing the mechanical L.M.N. unit in microns and by converting the energies relative to total transmission of the instrument at a given band without any film sample to percent transmission.

mix #7 5 gms of ethyl cellulose in 100 cc anhydrous toluene and 3 cc trimethylchlorosilane added

Silica Analysis

The silica content was determined from the dry film after leaching with 1:1 isopropyl acetate-solvesso* solution to remove any unreacted materials. One gram of the film may then be utilized for gravimetric analysis of silica by carefully melting down the film sample, wetting with 3 cc concentrated nitric acid, digesting for five minutes, then adding 1 cc concentrated sulfuric acid, digesting another five minutes, and finally igniting slowly to dryness. The residue by this method is pure white silica and the silica analyses noted below (page 21) were attained by this procedure.

Several other procedures (7)(8) for silica analysis were tried but either did not produce as white an ash or did not give the accuracy of the method described.

The silica analyses were standardized against pure distilled tetraethyl orthosilicate.

*solvesso- petroleum ether cut (b.p.79-81 C)

(Transmission)

1–15 μ

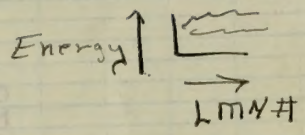
red – energy ref.

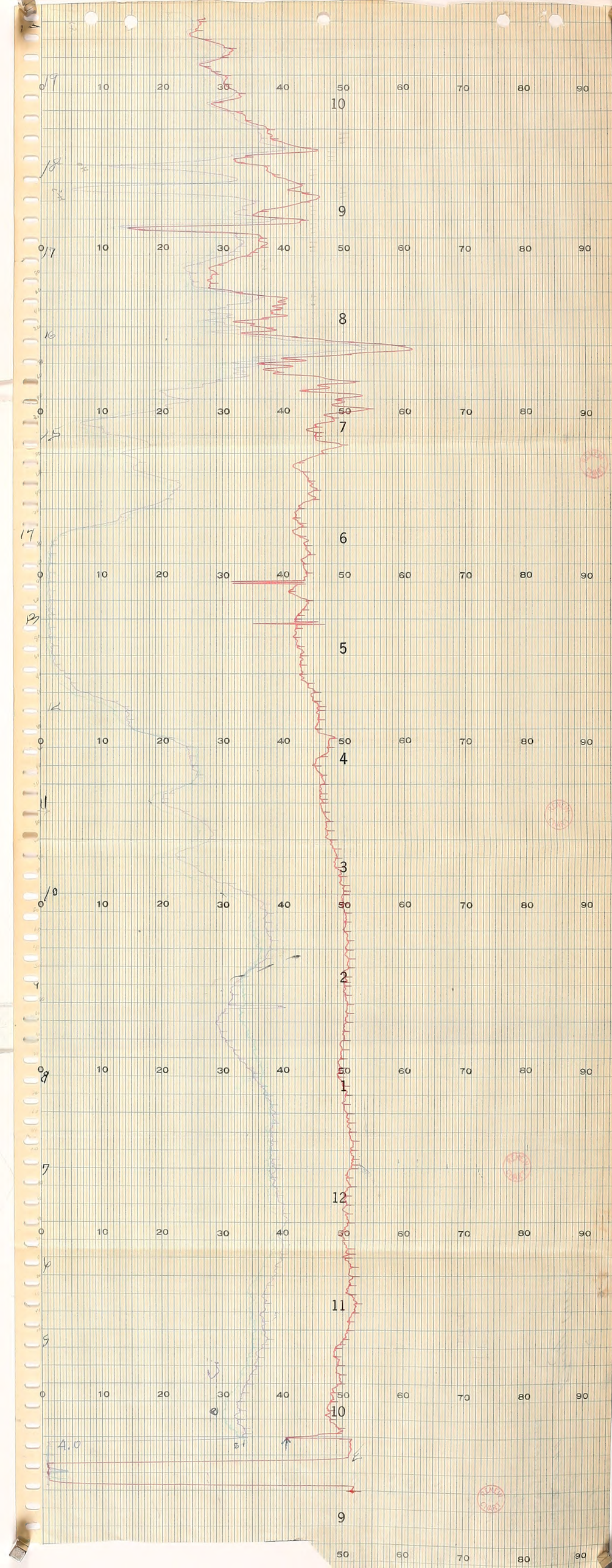
blue – mix #12 of #11

green – Dow ecel 10cps med

Energy curves

	LMN
1 μ	19.525
2	18.37
3	17.80
8	14.41
10	12.16
12	9.35
14	5.96




10
9
8
7
6
5
4
3
2
1
12
11
10
9
4.0

Perkin Elmer Spectrophotometer

Transmission Data Transcribed

from Energy Curves

Sample a = Dow ethyl cellulose Sample b = film #2

Slit mm	L.M.#	Microns	cm^{-1}	% Trans. by Recorder	Slit mm	L.M.#	Microns	cm^{-1}	% Trans. by Recorder
				b) purple #17 ↓ % trans / a green cel ↓ % trans		4.78	14.65	683	
						4.88	14.60	685	36.0/48.5 74% / 34.0/48.5 70%
						4.97	14.55	687	
						5.06	14.50	690	33.0/49.5 75% / 35.0/49.5 71%
						5.15	14.45	692	
						5.24	14.40	694	36.5/51.0 73% / 35.0/51.0 69%
						5.34	14.35	697	
						5.44	14.30	699	37.0/52.0 71% / 34.5/52.0 66%
				b / a		5.53	14.25	702	
						5.62	14.20	704	37.0/50.5 73% / 34.5/50.5 68%
						5.71	14.15	707	
				← #17 energy ← energy std ← cel energy		5.80	14.10	709	38.5/51.5 / 36.5/51.5
	4.13	15.00	667	32.5/49.0 68% / 31.0/49.0 63% ← % trans		5.90	14.05	712	75% / 71%
	4.22	14.95	669						
	4.32	14.90	671	33.0/49.5 69% / 30/47.5 63%					
	4.41	14.85	673						
	4.50	14.80	676	33.5/48.0 70% / 31.5/48.0 66%					
	4.59	14.75	678						
	4.69	14.70	680	35.0/49.5 71% / 33.0/49.5 67%					

Transmission Data

Sheet No. 2
of

SPECTROPHOTOMETRIC REPORT

Test No.

Sample No.

Date:

Description:

Tested by:

Reflection Corrected: ☐

Originator: B/R C/R

Reflection Not Corrected: B/R C/R

slit mm	L.M.#	Microns	cm^{-1}	% trans.	by recorder	slit mm	L.M.#	Microns	cm^{-1}	% trans.	by recorder
	5.96	14.00	714.3	39.5/51.0 77%	37.0/51.0 72%		7.69	13.05	766.3		
	6.06	13.95	716.8				7.77	13.00	769.2	37.0/50 73%	37.0/50 73%
	6.16	13.90	719.4	40.0/51.5 78%	38.0/50.5 75%		7.85	12.95	772.2		
	6.26	13.85	722.0				7.93	12.90	775.2	36/50.0 73%	37/50 74%
	6.36	13.80	724.6	40.0/50.5 79%	39.0/50.5 77%		8.01	12.85	778.2		
	6.46	13.75	727.3				8.09	12.80	781.3	34.5/49.5 70%	36.5/49.5 74%
	6.55	13.70	729.9	40.0/50.0 80%	38/50.0 76%		8.17	12.75	784.3		
	6.65	13.65	732.6				8.25	12.70	787.4	32.5/49.5 66%	35.5/49.5 72%
	6.74	13.60	735.3	39.0/50.5 77%	37.5/50.5 74%		8.33	12.65	790.5		
	6.83	13.55	738.0				8.41	12.60	793.7	30/50 61%	35/50 70%
	6.92	13.50	740.7	38.5/51.0 75%	38.0/51.0 74%		8.49	12.55	796.8		
	7.01	13.45	743.5				8.57	12.50	800.0	29/50 58%	33.5/50 67%
	7.10	13.40	746.3	38.5/51.5 75%	37.5/51.5 73%		8.64	12.45	803.2		
	7.19	13.35	749.1				8.72	12.40	806.5	30/50.5 60%	33/50 65%
	7.27	13.30	751.9	38.0/51.5 74%	37.5/51.5 73%		8.80	12.35	809.7		
	7.36	13.25	754.7				8.88	12.30	813.0	31.5/50.5 62%	33.5/50.5 66%
	7.44	13.20	757.6	38.0/51.0 74%	37.0/51.0 72%		8.96	12.25	816.3		
	7.52	13.15	760.5				9.04	12.20	819.7	32.5/50.5 64%	33/50.5 65%
	7.61	13.10	760.5	39.0/50.5 77%	38.0/50.5 75%		9.12	12.15	823.0		

Sheet No. 3
of

Transmission Data

Test No.

SPECTROPHOTOMETRIC REPORT

Sample No.

Date:

Description:

Tested by:

Reflection Corrected: ☐

Originator: B/R B/R

Reflection Not Corrected: B/R C/R ☐

slit mm.	L.M.#	Microns	cm^{-1}	% trans.	% by recorder	slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder
	9.19	12.10	826.4	35.5/51.0 70%	35.0/51.0 69%		10.62	11.15	896.9		
	9119										
	9.27	12.05	829.9				10.69	11.10	900.9	28/47.0 60%	26.0/47.0 55%
	9.35	12.00	833.3	37.5/50.5 74%	36.0/50.5 71%		10.76	11.05	905.0		
	9.43	11.95	836.8				10.84	11.00	909.1	25.5/47.5 54%	23.0/47.5 48%
	9.50	11.90	840.3	38.0/50.5 75%	36.0/50.5 71%		10.91	10.95	913.2		
	9.58	11.85	843.9				10.98	10.90	917.4	20/46.0 44%	18.5/46.0 40%
	9.66	11.80	847.5	37.0/50.5 73%	34.5/50.5 68%		11.05	10.85	921.7		
	9.73	11.75	851.1				11.12	10.80	925.9	21.5/46.0 47%	19.5/46.0 42%
	9181	11.70	854.7	37/50.0 74%	35.0/50.0 70%		11.19	10.75	930.2		
	9.89	11.65	858.3				11.25	10.70	934.6	25.5/46.5 55%	26.0/46.5 55%
	9.96	11.60	862.1	35.5/50.0 71%	32.5/50.0 65%		11.32	10.65	939.0		
	10.03	11.55	865.8				11.38	10.60	943.4	26.0/46.5 55%	26.0/45.5 57%
	10.11	11.50	869.6	36.0/50.0 72%	27.5/50.0 55%		11.45	10.55	947.9		
	10.18	11.45	873.3				11.52	10.50	952.4	24.5/46.5 53%	26.0/46.5 56%
	10.26	11.40	877.2	26.0/49.0 53%	22.0/49.0 45%		11.58	10.45	956.9		
	10.33	11.35	881.1				11.65	10.40	961.5	23.0/47.5 48%	24.0/47.5 50%
	10.40	11.30	885.0	23.0/49.0 47%	19.5/49.0 40%		11.71	10.35	966.2		
	10.48	11.25	888.9				11.78	10.30	970.9	16.5/45.5 34%	15.5/45.5 34%
	10.55	11.20	892.9	27.0/48.0 56%	24.0/48.0 50%		11.84	10.25	975.6		

Sheet No. 4
of

Transmission Data

Test No.

SPECTROPHOTOMETRIC REPORT

Sample No.

Date:

Description:

Tested by:

Reflection Corrected:

Originator: B/R C/R

Reflection Not Corrected: 13/12 4/R

Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder	Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder
	11.91	10.20	980.4	1.5/46.0 32%	1.0/46.0 28%		13.06	9.25	1081		
	11.97	10.15	985.2				13.12	9.20	1087	1.5/43.5 3%	1.5/43.5 3%
	12.03	10.10	990.1	1.5/46.0 32%	1.0/46.0 26%		13.17	9.15	1093		
	12.10	10.05	995.0				13.23	9.10	1099	1.5/43.5 3%	1.5/43.5 3%
	12.16	10.00	1000	9.5/45.0 21%	7.5/45.0 17%		13.28	9.05	1105		
	12.22	9.95	1005				13.34	9.00	1111	1.5/41.5 4%	1.0/41.5 4%
	12.28	9.90	1010	5.0/44.0 11%	3.5/44.0 8%		13.40	8.95	1117		
	12.34	9.85	1015				13.45	8.90	1124	1.5/43.5 3%	1.0/43.5 3%
	12.41	9.80	1020	4.0/43.0 9%	2.5/43.0 6%		13.51	8.85	1130		
	12.47	9.75	1026				13.57	8.80	1136	1.5/43.5 3%	1.0/43.5 3%
	12.53	9.70	1031	2.5/43.0 6%	2.0/43.0 5%		13.62	8.75	1143		
	12.59	9.65	1036				13.68	8.70	1149	1.5/44.0 3%	1.5/44.0 3%
	12.65	9.60	1042	2.0/43.0 5%	1.5/43.0 3%		13.73	8.65	1156		
	12.71	9.55	1047				13.78	8.60	1163	1.5/44.0 3%	1.5/44.0 3%
	12.77	9.50	1053	1.5/42.0 4%	1.5/42.0 4%		13.84	8.55	1170		
	12.83	9.45	1058				13.89	8.50	1176	3.0/43.0 7%	3.0/43.0 7%
	12.88	9.40	1064	1.5/43.0 4%	1.0/42.0 2%		13.94	8.45	1183		
	12.94	9.35	1070				13.99	8.40	1190	7.0/42.5 16%	8.0/42.5 19%
	13.00	9.30	1075	1.5/42.0 4%	1.0/42.0 2%		14.05	8.35	1198		

Sheet No. 5
of

Transmission Data

Test No.

SPECTROPHOTOMETRIC REPORT

Sample No.

Date:

Description:

Tested by:

Reflection Corrected: ☐

Originators: B/R H/R

Reflection Not Corrected: B/R C/H ☐

Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder	Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder
	14.10	8.30	1205	13.0/42.0	15.0/42.0		15.21	7.16	1400	12.0/48.0	11.0/48.0
				31%	36%					25%	23%
	14.17	8.24	1214	15.0/42.0	17.0/42.0		15.26	7.10	1410	17.0/49.0	14.0/49.0
				36%	40%					35%	28%
	14.23	8.18	1222	19.0/43.0	20.0/43.0		15.31	7.04	1420	31.0/54.0	17.0/54.0
				44%	46%					39%	31%
	14.29	8.12	1231	20.0/44.5	21.0/44.5		15.35	7.00	1430	32.0/49.5	19.0/49.5
				46%	48%					44%	38%
	14.35	8.06	1241	21.5/44.5	21.5/44.5		15.39	6.96	1435	34.0/49.0	21.0/49.0
				48%	48%					49%	43%
	14.41	8.00	1250	22.0/45.5	21.0/45.5		15.42	6.92	1445	22.5/50.0	18.0/50.0
				48%	46%					45%	37%
	14.47	7.94	1260	22.5/44.5	20.0/44.5		15.45	6.88	1450	24.0/53.0	17.0/53.0
				50%	45%					40%	32%
	14.53	7.88	1270	21.0/44.0	18.0/44.0		15.49	6.84	1460	31.0/43.0	17.0/43.0
				48%	41%					49%	40%
	14.59	7.82	1280	17.0/43.5	16.0/43.5		15.52	6.80	1470	31.0/44.0	18.0/44.0
				39%	34%					47%	41%
	14.65	7.76	1290	13.5/42.0	13.5/42.0		15.56	6.76	1480	27.0/46.0	24.0/46.0
				37%	32%					37%	52%
	14.71	7.70	1300	16.5/43.0	14.0/43.0		15.59	6.72	1490	29.0/52.0	26.0/52.0
				38%	32%					56%	50%
	14.76	7.64	1310	15.0/45.0	12.0/45.0		15.62	6.68	1500	29.5/46.0	26.0/49.0
				33%	27%					60%	53%
	14.82	7.58	1320	13.5/46.5	10.5/46.5		15.66	6.64	1505	32.5/45.0	31.5/45.0
				29%	22%					77%	70%
	14.86	7.52	1330	18.0/49.5	14.0/49.5		15.69	6.60	1515	33.5/39.5	30.5/39.5
				36%	28%					85%	77%
	14.93	7.46	1340	17.5/49.0	13.5/49.0		15.72	6.56	1525	33.0/37.5	29.5/37.5
				36%	28%					88%	79%
	14.99	7.40	1350	14.0/45.5	10.5/45.5		15.76	6.52	1535	32.0/40.0	32.0/40.0
				31%	22%					85%	80%
	15.04	7.34	1360	10.5/45.5	7.5/45.5		15.79	6.48	1545	32.0/36.0	27.5/32.0
				23%	16%					89%	82%
	15.10	7.28	1370	10.0/45.5	7.0/46.5		15.82	6.44	1555	32.5/38.0	32.5/38.0
				22%	15%					86%	86%
	15.15	7.22	1385	6.5/46.0	5.0/46.0		15.85	6.40	1565	32.0/40.0	33.0/46.0
				22%	11%					90%	82%

Sheet No. 6
of

Transmission Data

SPECTROPHOTOMETRIC REPORT

Test No.

Sample No.

Date:

Description:

Tested by:

Reflection Corrected:

Originator: B/R C/R

Reflection Not Corrected: B/R C/R

Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder	Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder
	15.88	6.36	1570	42.0/48.0	42.0/48.0		16.44	5.60	1785	31.0/39.0	37.0/39.0
				83%	87%					79%	74%
	15.91	6.32	1580	42.0/52.0	45.0/52.0		16.46	5.56	1800	32.0/40.5	33.0/40.5
				81%	86%					81%	81%
	15.94	6.28	1590	53.5/61.0	49.0/61.0		16.49	5.52	1810	34.5/39.5	35.0/39.5
				88%	80%					87%	81%
	15.97	6.24	1600	53.0/60.0	48.0/60.0		16.52	5.48	1825	34.5/40.0	34.5/40.0
				88%	80%					89%	86%
	16.00	6.20	1610	52.0/57.0	44.5/59.0		16.55	5.44	1840	37.0/37.0	33.0/37.0
				88%	80%					100%	89%
	16.03	6.16	1625	50.0/57.0	43.0/57.0		16.57	5.40	1850	35.0/35.0	32.0/35.0
				88%	75%					100%	86%
	16.06	6.12	1635	41.0/48.0	36.5/48.0		16.60	5.36	1865	34.0/31.5	28.0/31.5
				85%	76%					95%	84%
	16.09	6.08	1645	35.0/41.0	32.5/41.0		16.63	5.32	1880	27.0/28.0	24.0/28.0
				85%	78%					96%	86%
	16.12	6.04	1655	33.0/37.5	29.5/37.5		16.65	5.28	1895	25.0/25.0	24.0/25.0
				88%	79%					91%	86%
	16.15	6.00	1670	22.5/34.0	27.0/34.0		16.68	5.24	1910	25.0/28.0	24.0/26.0
				84%	79%					89%	86%
	16.18	5.96	1680	33.0/38.5	31.5/38.5		16.70	5.20	1920	28.0	24.0/26.0
				87%	82%					89%	86%
	16.21	5.92	1690	33.0/36.0	30.5/36.0		16.73	5.16	1940	24.0/28.5	23.0/26.5
				92%	85%					86%	81%
	16.24	5.88	1700	30.0/35.0	28.0/35.0		16.75	5.12	1950	25.0/26.0	23.0/28.0
				87%	80%					89%	82%
	16.26	5.84	1710	29.5/32.5	27.5/32.5		16.78	5.08	1970	24.5/28.0	23.5/27.0
				91%	82%					84%	81%
	16.29	5.80	1725	31.0/37.0	29.5/37.0		16.80	5.04	1980	24.0/28.0	23.0/27.0
				84%	78%					84%	81%
	16.32	5.76	1735	31.0/40.0	30.5/40.0		16.83	5.00	2000	24.0/28.0	23.5/27.0
				77%	76%					86%	80%
	16.35	5.72	1750	30.0/38.0	28.0/38.0		16.85	4.96	2020	24.0/28.0	23.0/27.0
				79%	74%					86%	78%
	16.38	5.68	1760	28.0/38.0	27.0/38.0		16.88	4.92	2030	24.0/28.5	22.5/27.5
				74%	79%					84%	79%
	16.41	5.64	1775	29.5/39.5	29.0/39.5		16.90	4.88	2050	25.0/28.0	23.5/27.5
				75%	75%					86%	79%

Sheet No. 7
of

Transmission Data

Test No.

SPECTROPHOTOMETRIC REPORT

Sample No.

Date:

Description:

Tested by:

Reflection Corrected: ☐

Originator: B/R 4/R

Reflection Not Corrected: B/R 4/R ☒

Slit mm.	L.M.#	Microns	cm⁻¹	% Trans.	% by Recorder	Slit mm.	L.M.#	Microns	cm⁻¹	% Trans.	% by Recorder
	16.93	4.84	2070	27.0/31.0	25.0/31.0		17.37	4.08	2450	38.0/43.0	35.5/43.0
				87%	81%					88%	82%
	16.95	4.80	2080	28.0/31.5	26.0/31.5		17.40	4.04	2480	38.5/43.5	35.0/43.5
				89%	83%					88%	80%
	16.98	4.76	2100	30.0/34.0	28.0/34.0		17.42	4.00	2500	38.0/38.0	35.0/38.0
				88%	82%					100%	87%
	17.00	4.72	2120	31.0/34.0	28.0/34.0		17.44	3.96	2530	34.0/35.0	30.0/35.0
				91%	82%					97%	86%
	17.03	4.68	2140	31.5/35.0	28.0/35.0		17.46	3.92	2550	32.0/35.5	30.0/35.5
				90%	84%					90%	84%
	17.05	4.64	2160	32.0/35.0	29.0/35.0		17.48	3.88	2580	32.5/37.0	30.5/37.0
				91%	83%					88%	82%
	17.07	4.60	2170	32.0/35.5	28.0/35.5		17.50	3.84	2600		
				90%	79%						
	17.10	4.56	2190	32.5/36.5	29.0/36.5		17.52	3.80	2630		
				89%	79%						
	17.12	4.52	2210	33.0/37.0	29.5/37.0		17.54	3.76	2660		
				89%	80%						
	17.15	4.48	2230	33.0/37.5	29.5/37.5		17.56	3.72	2690		
				89%	79%						
	17.17	4.44	2250	33.0/36.0	29.0/36.0		17.58	3.68	2720	35.5/44.0	32.5/44.0
				92%	80%					81%	74%
	17.20	4.40	2270	32.5/34.5	29.0/36.5		17.60	3.64	2750	35.5/44.0	32.0/44.0
				89%	79%					81%	73%
	17.22	4.36	2290	32.0/36.0	29.0/36.0		17.62	3.60	2780	34.0/45.0	29.0/45.0
				89%	80%					75%	64%
	17.24	4.32	2310	32.5/35.0	29.0/35.0		17.64	3.56	2810	33.0/44.0	27.5/44.0
				93%	83%					72%	60%
	17.26	4.28	2340	30.0/30.0	30.0/30.0		17.66	3.52	2840	30.0/46.0	27.0/46.0
				100%	100%					69%	63%
	17.29	4.24	2360	14.0/14.5	12.0/14.5		17.68	3.48	2870	26.0/44.0	19.6/44.0
				96%	83%					59%	47%
	17.31	4.20	2380	13.0/15.0	11.5/15.0		17.70	3.44	2910	15.0/43.0	9.0/43.0
				87%	77%					35%	21%
	17.33	4.16	2400	14.0/22.0	11.0/22.0		17.72	3.40	2940	8.0/41.0	5.0/41.0
				64%	77%					20%	10%
	17.35	4.12	2430	29.0/46.0	32.0/46.0		17.73	3.36	2980	5.0/41.0	3.5/41.0
				72%	80%					12%	8%

Sheet No. 8
of

Transmission Data

Test No.

SPECTROPHOTOMETRIC REPORT

Sample No.

Date:

Description:

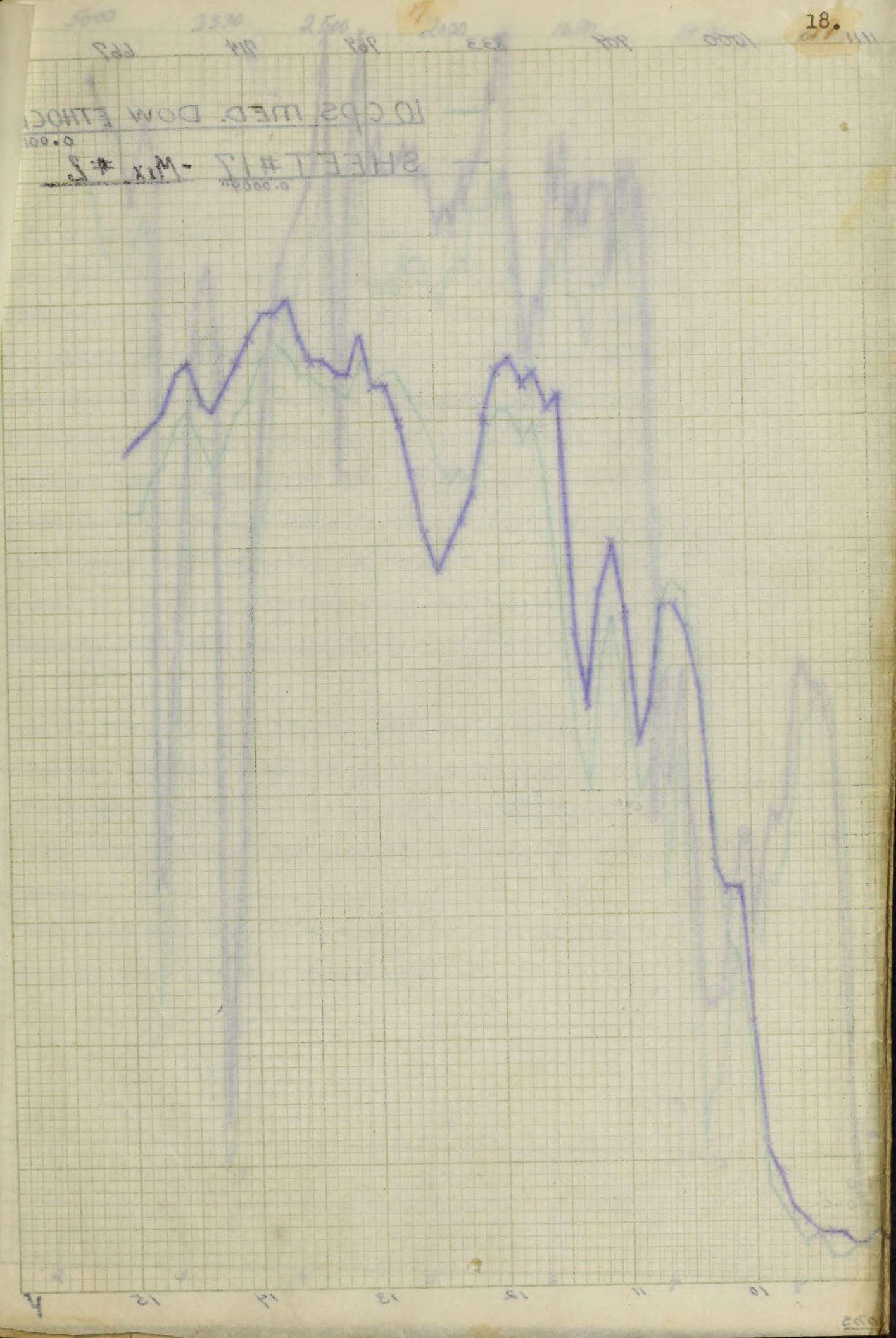
Tested by:

Reflection Corrected: ☐

Originator: B/R E/R

Reflection Not Corrected: B/R ☐ E/R

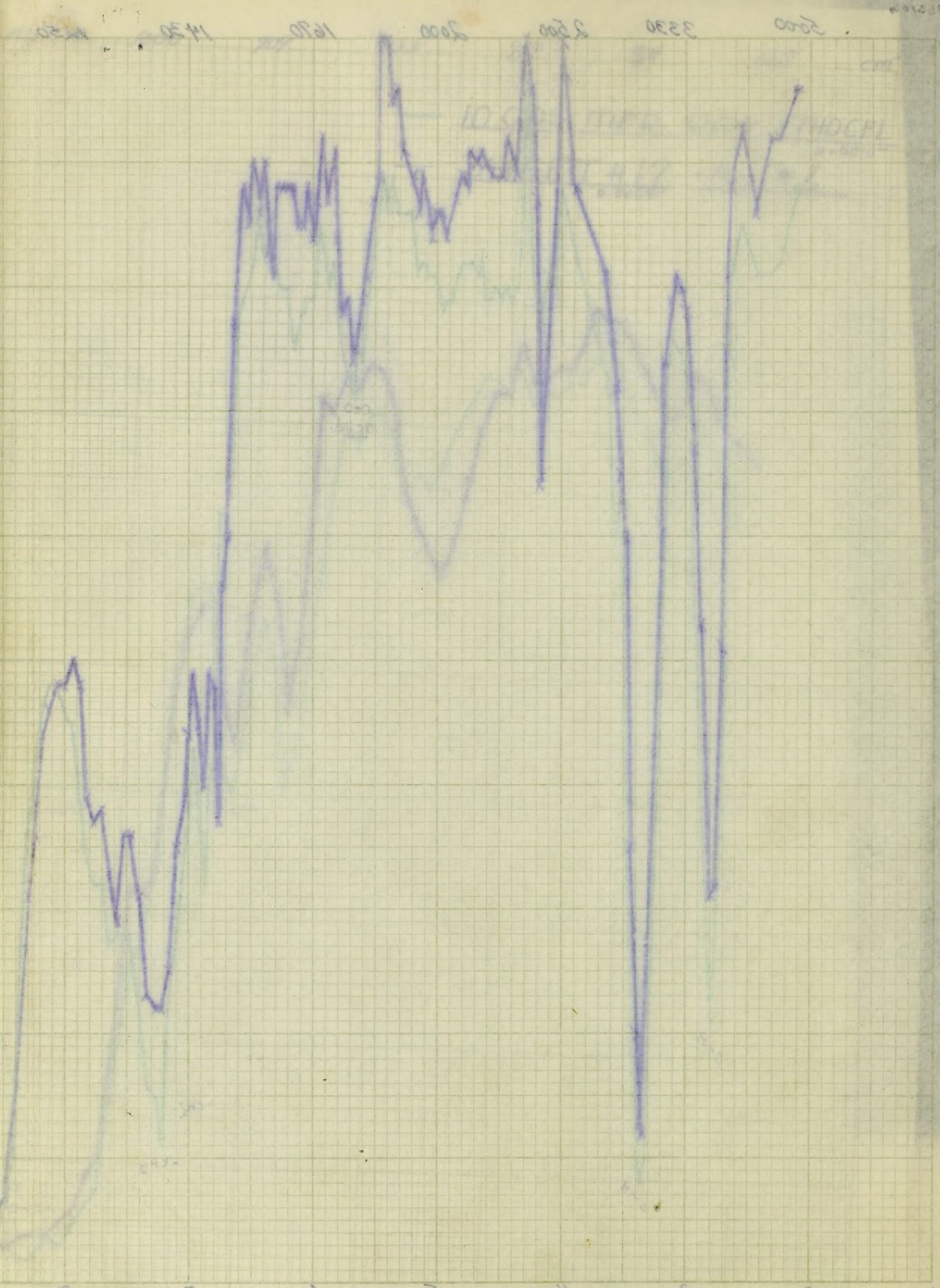
Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder	Slit mm	L.M.#	Microns	cm^{-1}	% trans.	% by recorder
	17.75	3.32	3010	5.0/42.0	4.0/42.0		18.10	2.56	3910	31.5/34.0	29.0/34.0
				12%	10%					93%	85%
	17.77	3.28	3050				18.12	2.52	3970		
	17.79	3.24	3090				18.13	2.48	4030		
	17.80	3.20	3130	26.0/42.5	26.0/42.5		18.15	2.44	4100	37.0/43.0	35.0/43.0
				61%	61%					86%	81%
	17.82	3.16	3160	31.0/42.0	30.0/42.0		18.17	2.40	4170		
				74%	71%						
	17.84	3.12	3210	32.5/41.0	31.0/41.0		18.19	2.36	4240	40.5/45.0	36.5/45.0
				79%	69%					90%	81%
	17.86	3.08	3250	32.5/40.0	30.0/40.0		18.21	2.32	4310	34.5/43.0	33.0/43.0
				81%	75%					92%	81%
	17.88	3.04	3290	31.0/38.5	29.0/38.5		18.23	2.28	4390		
				80%	75%						
	17.90	3.00	3330	30.0/38.5	28.0/38.5		18.25	2.24	4460	37.9/40.0	33.0/40.0
				78%	72%					92%	82%
	17.91	2.96	3380				18.27	2.20	4550		
	17.93	2.92	3420	25.0/37.5	21.0/37.5		18.29	2.16	4630	36.5/38.0	33.5/38.0
				67%	56%						
	17.95	2.88	3470	20.0/37.5	15.0/37.5		18.31	2.12	4720	96%	88%
				53%	40%						
	17.97	2.84	3520				18.33	2.08	4810	36.5/38.0	33.5/38.0
										96%	88%
	17.99	2.80	3570	11.5/37.5	8.0/37.5		18.35	2.04	4900		
				31%	21%						
	18.00	2.76	3620	11.2/36.5	10.1/36.5		18.37	2.00	5000		
				32%	27%						
	18.02	2.72	3680	18.0/35.0	18.0/35.0						
				51%	51%						
	18.04	2.68	3730	24.0/32.0	24.0/32.0						
				75%	75%						
	18.06	2.64	3790	28.0/32.0	26.0/32.0						
				88%	81%						
	18.08	2.60	3850	29.4/32.0	26.5/32.0						
				91%	83%						



% Transmission

— 10 CPS MED. DOW ETHOCEL 0.502"

— SHEET #17 - MIX #2 0.502"



Discussion of Results

By a comparison of the two curves of the spectrograph (page 18) it will be seen that there is no significant difference in absorption if a visual correction is made for a slight apparent difference in film thicknesses. Therefore, it is concluded that in general no reaction detectable by infra-red spectroscopy has occurred, and in particular that the hydroxyl group of the ethyl cellulose has not been attacked. This is further supported by lack of any change in flexibility and hardness of film #2 as compared to the straight ethyl cellulose because any cross linkage by tetraethyl orthosilicate would embrittle the film.

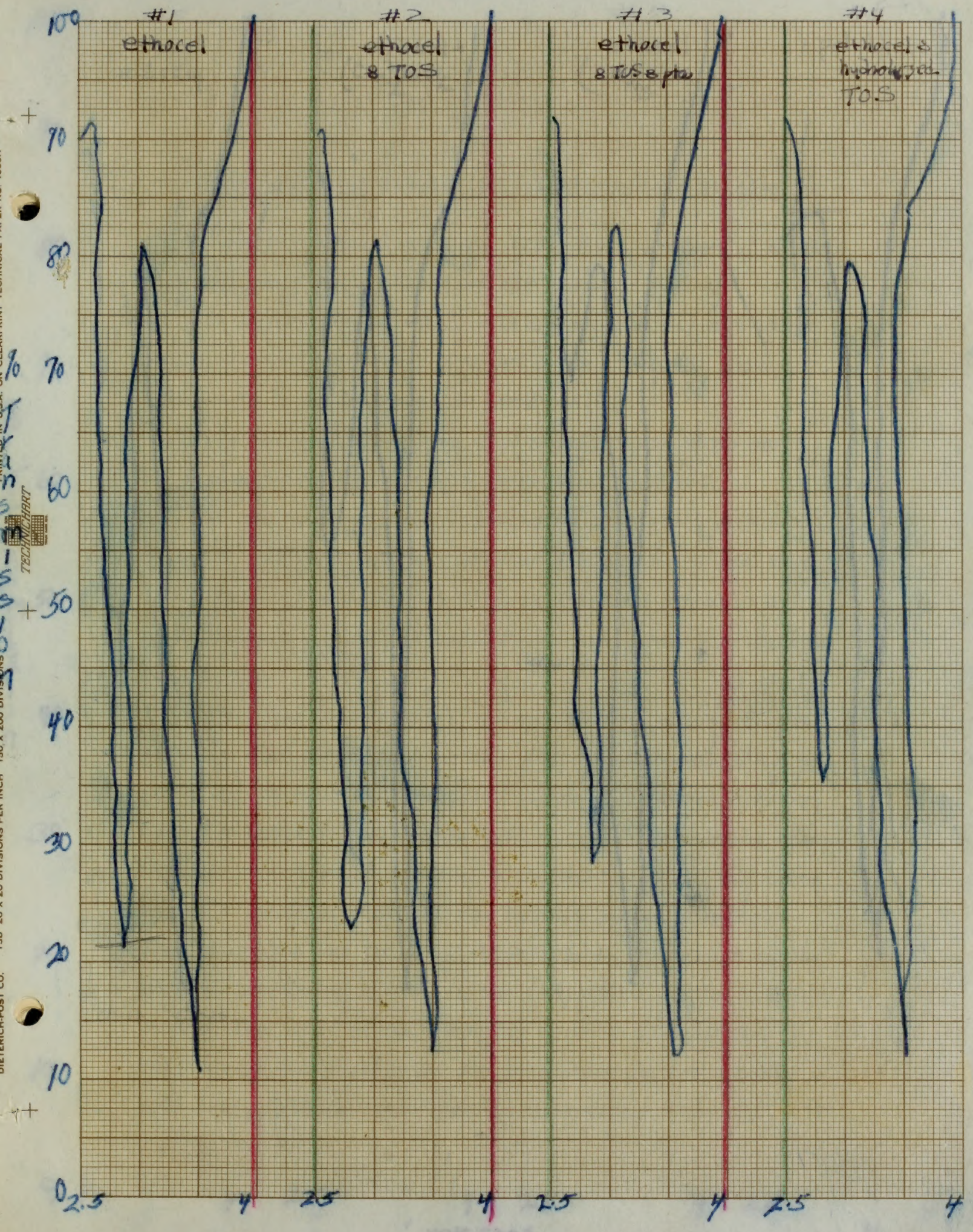
Since the following studies show that reactions with the polymer hydroxyl group are detectable by infra-red spectroscopy, it must be that no reaction ~~has~~ occurred between ethyl cellulose and unmodified tetraethyl orthosilicate.

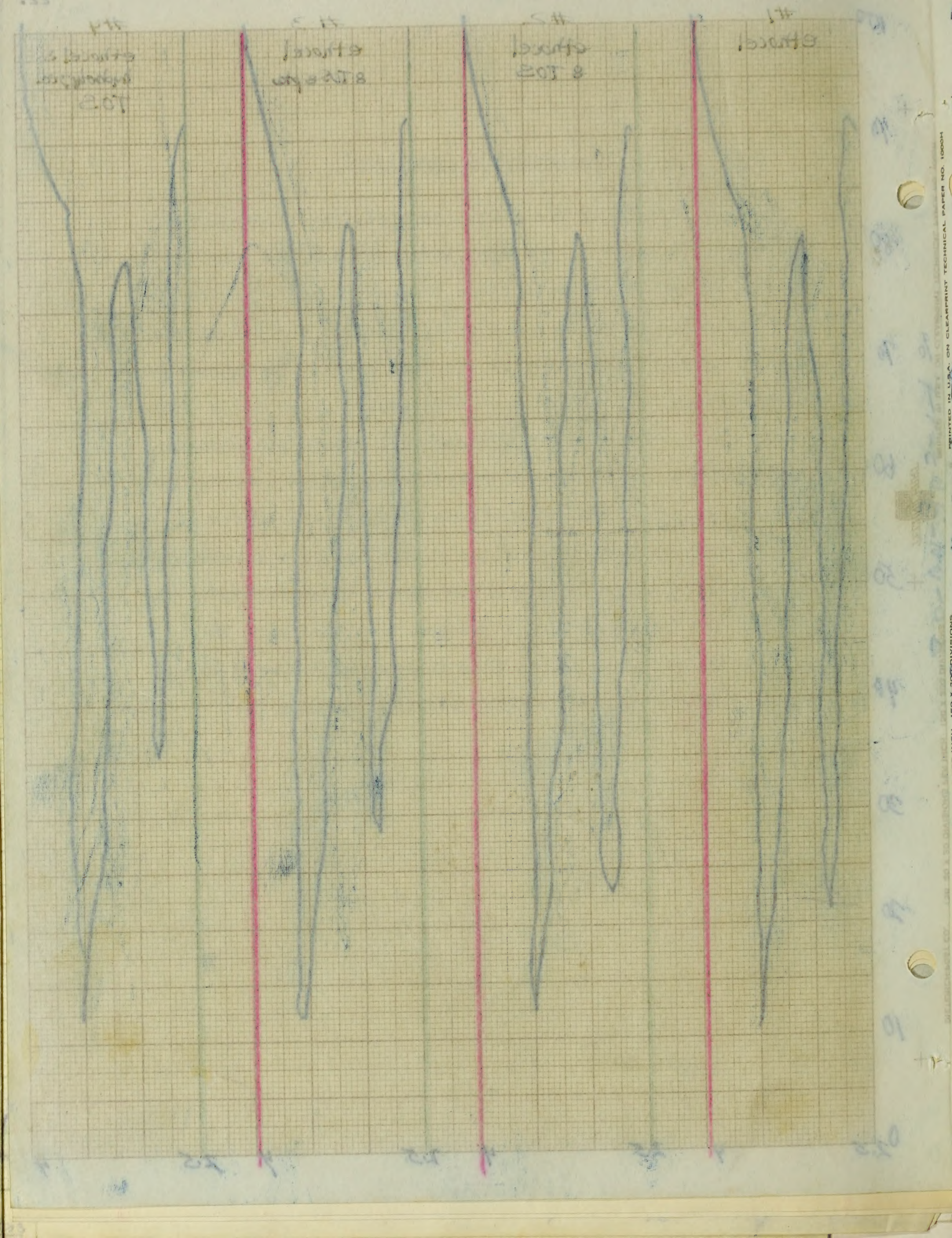
Some inversion in the relative absorptions of the two films is probably due to the tetraethyl orthosilicate.

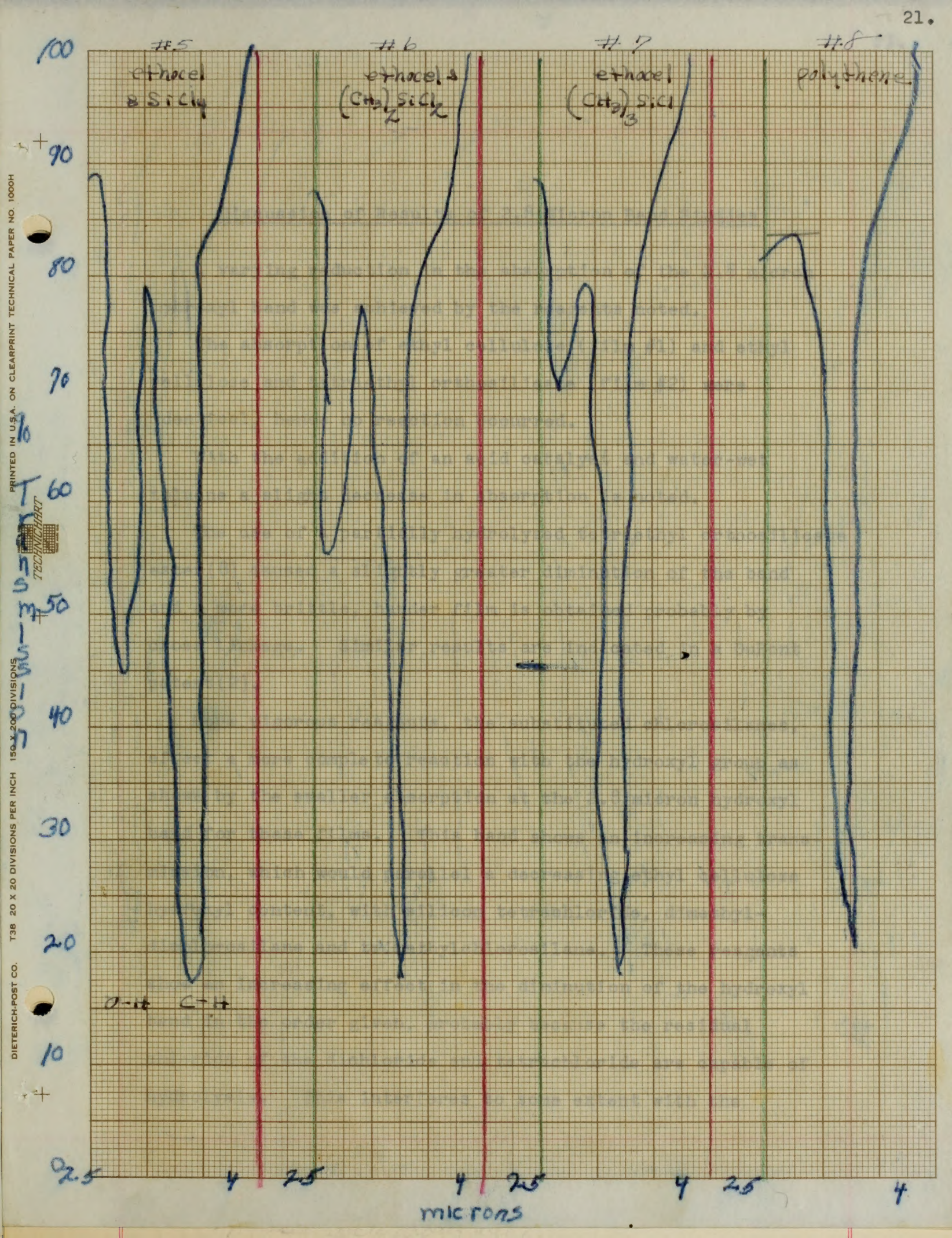
Spectrographs (continued)

With reference to the films prepared from mixes three to seven (see pages 5 and 6), these are studied only in the 2.5 to 4.0 micron band since the modification of the ethyl cellulose structure primarily involves the 2.8 micron band of hydroxyl absorption. In each graph, the 3.4 carbon-hydrogen band is included as a reference. Cure #1 is that of the ethyl cellulose of 0.52 hydroxyl groups per glucose unit and curve #8 is that of polyethylene which contains no hydroxyl groups. The absorptions of these two curves at 2.8 microns are used as limiting points in the development of formula for expressing the 2.8 micron transmission as the residual hydroxyl groups per glucose unit (see page 26).

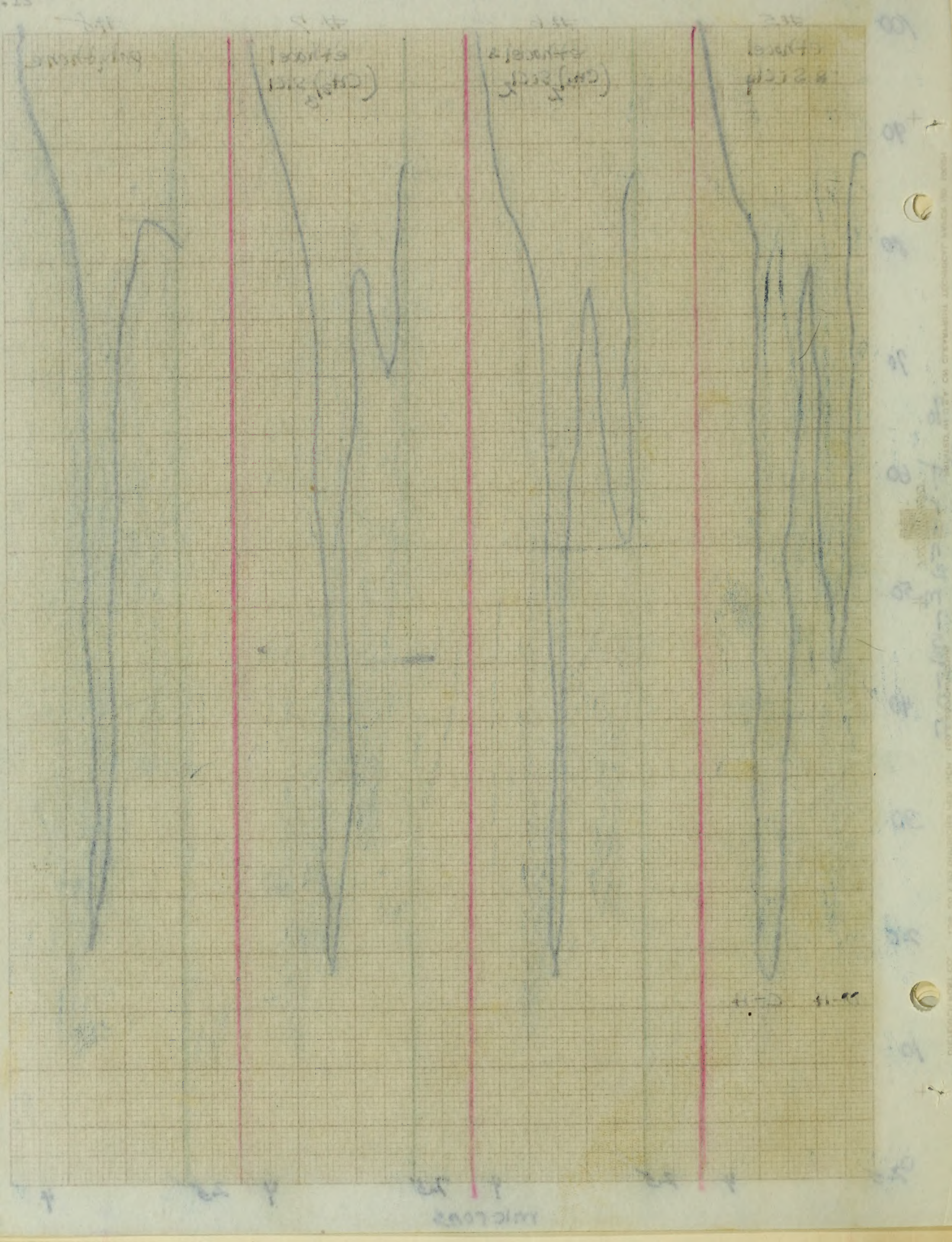
The transmission curves that follow are numbered to correspond to the mix and film described on page 5.


#1
ethocel
#2
ethocel
& TOS
#3
ethocel
& TOS & plas
#4
ethocel & hydrolyzed
TOS
100
70
80
70
60
50
40
30
20
10
0
2.5
4
2.5
4
2.5
4
2.5
4





DIETERICH-POST CO. T38 20 X 20 DIVISIONS PER INCH 150 X 200 DIVISIONS PRINTED IN U.S.A. ON CLEARPRINT TECHNICAL PAPER NO. 1000H
TECHNICHART



Discussion of Results of 2.8 Micron Band Studies

A varying reduction in the absorption of the 2.8 micron hydroxyl band was achieved by the reagents noted.

The absorption of ethyl cellulose (film #1) and ethyl cellulose and tetraethyl orthosilicate (film #2) were identical, hence no reaction occurred.

With the addition of an acid catalyst and water-wet toluene a slight decrease in absorption is noted.

The use of a partially hydrolyzed tetraethyl orthosilicate ester(8) caused a slightly greater diminution of the band and a more brittle, harder film is obtained probably by cross linkage. Similar results are indicated in a DuPont patent(2).

More vigorous reagents, the substituted chlorosilanes, effect a more complete reaction with the hydroxyl group as shown by the smaller absorption at the 2.8 micron hydroxyl band for these films. This band shows an increasing transmission, which would parallel a decreasing ethyl cellulose hydroxyl content, with silicon tetrachloride, dimethyldichlorosilane and trimethylchlorosilane. These reagents show an increasing effect in the diminution of the hydroxyl band in the order given, probably because the residual chloride of the dichloride and tetrachloride are capable of hydrolysis. This interferes to some extent with the

comparison of polymer hydroxyl to silica content since the Perkin-Elmer spectrophotometer used does not distinguish between the carbon hydroxyl and the silicon hydroxyl. Since this is probably not a major error, no corrections are made nor appear possible.

It was also observed that imbibition of film #2 in isopropyl alcohol saturated with HCl for 30 minutes produced a product which when baked at 120°C for 20 minutes became hard and brittle. Since this process would serve to hydrolyze the tetraethyl orthosilicate to a partial ester of silicic acid, it is concluded that hydroxyl groups must be introduced into tetraethyl orthosilicate to enable reaction with the hydroxyl group of ethyl cellulose.

Analysis Formula for Hydroxyl by Transmission at 2.8 Micron Band

Since the efficiency of the reagent in modifying the polymer is proportional to the decrease in absorption due to the polymer hydroxyl group, a method may be developed for determining the residual hydroxyl content per glucose unit from the 2.8 micron transmission magnitude. Other sources(9)(10) have applied infra-red spectroscopy to analyze polymer modifications.

Since the film absorption follows Beer's law ($-\log T = kC$ where T = transmission, k = a constant and C = concentration) and since the concentration here refers to the hydroxyl content per glucose unit, a formula may be derived to express percent transmission as the residual hydroxyl content per glucose unit. Applying Beer's law and the 2.8 micron transmission data should allow the plotting of a curve relating the transmission to hydroxyl groups per glucose unit since it is known that the untreated ethyl cellulose has 0.52 hydroxyl groups and polyethylene zero hydroxyl groups per glucose unit.

Let T_o = transmission at maximum hydroxyl content

T_m = " " zero " "

T = " of 2.8 micron band

$(OH)_T$ = residual hydroxyl groups per glucose unit

Since the 2.8 micron transmission of polyethylene (film #8) is 82% and the unmodified ethyl cellulose (film #1) transmits 22%, the equation must be modified so that these limits correspond to zero and 0.52 hydroxyl groups per glucose unit. Then,

$$(OH)_T = \frac{\log T_o}{\log T} \times a - b, \quad \frac{\log T_o}{\log T_m} \times a = b, \quad a - b = 0.5$$

$$a = 0.83 \qquad b = 0.31$$

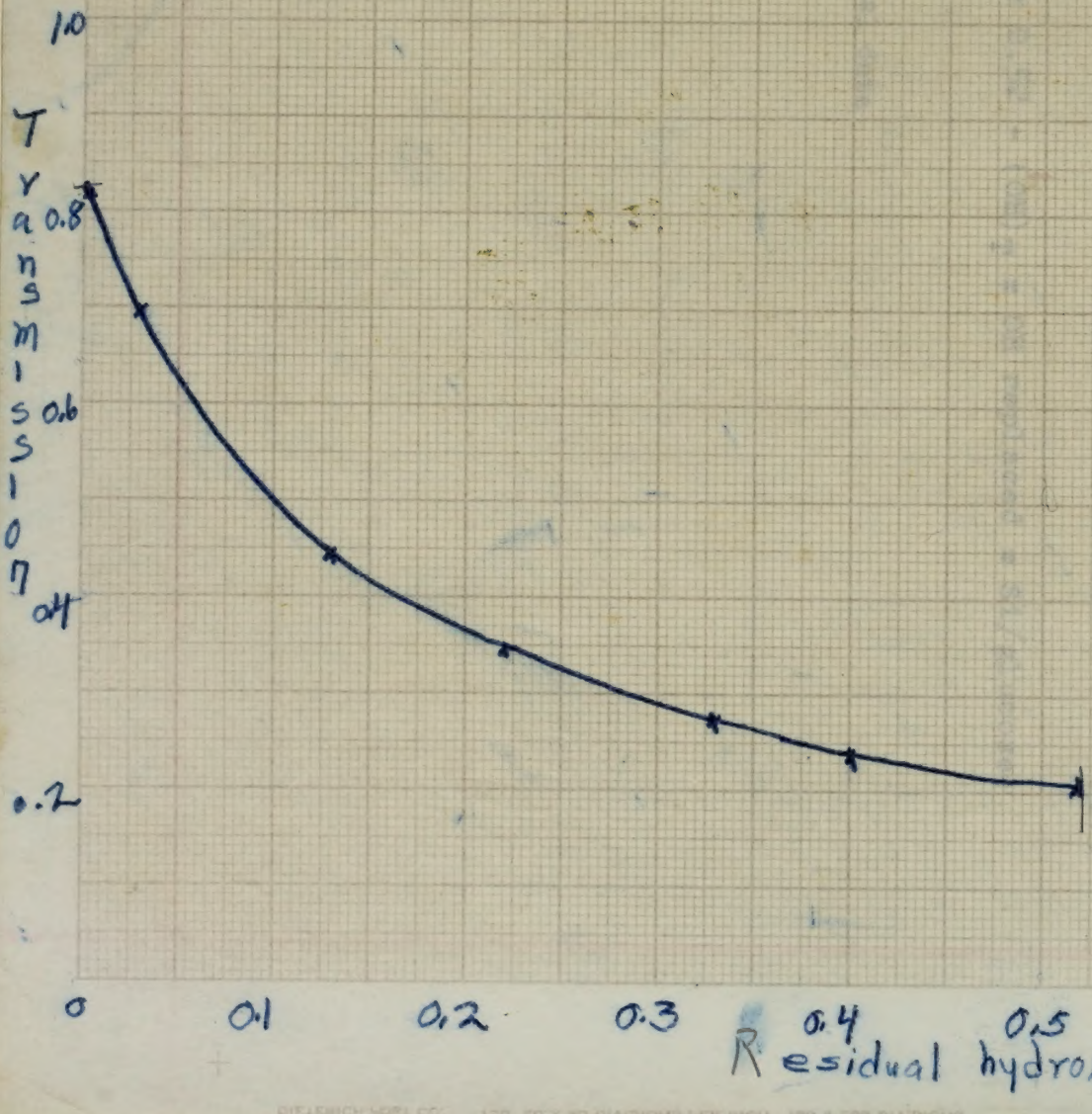
$$(OH)_T = \frac{\log T_o}{\log T} \times 0.83 - 0.31$$

This derived equation allows the expression of percent transmission in terms of residual hydroxyl groups per glucose unit and this data is tabulated in the following table.

Film No.	T	log T	Calculated $(OH)_T$
8	82	.9138	0
7	70	.8451	0.03
6	45	.6532	0.13
5	35	.5441	0.22
4	28	.4472	0.33
3	25	.3979	0.40
1	22	.3424	0.52

This calculated residual hydroxyl content is plotted against the observed transmission in the attached graph.

$$[OH]_T = \left[\frac{\log \frac{1}{T_0}}{\log T}\right] \times 0.83 - 0.31$$



DIETERICH-POST CO. T38 20 X 20 DIVISIONS PER INCH 150 X 200 DIVISIONS
TECHNICHART
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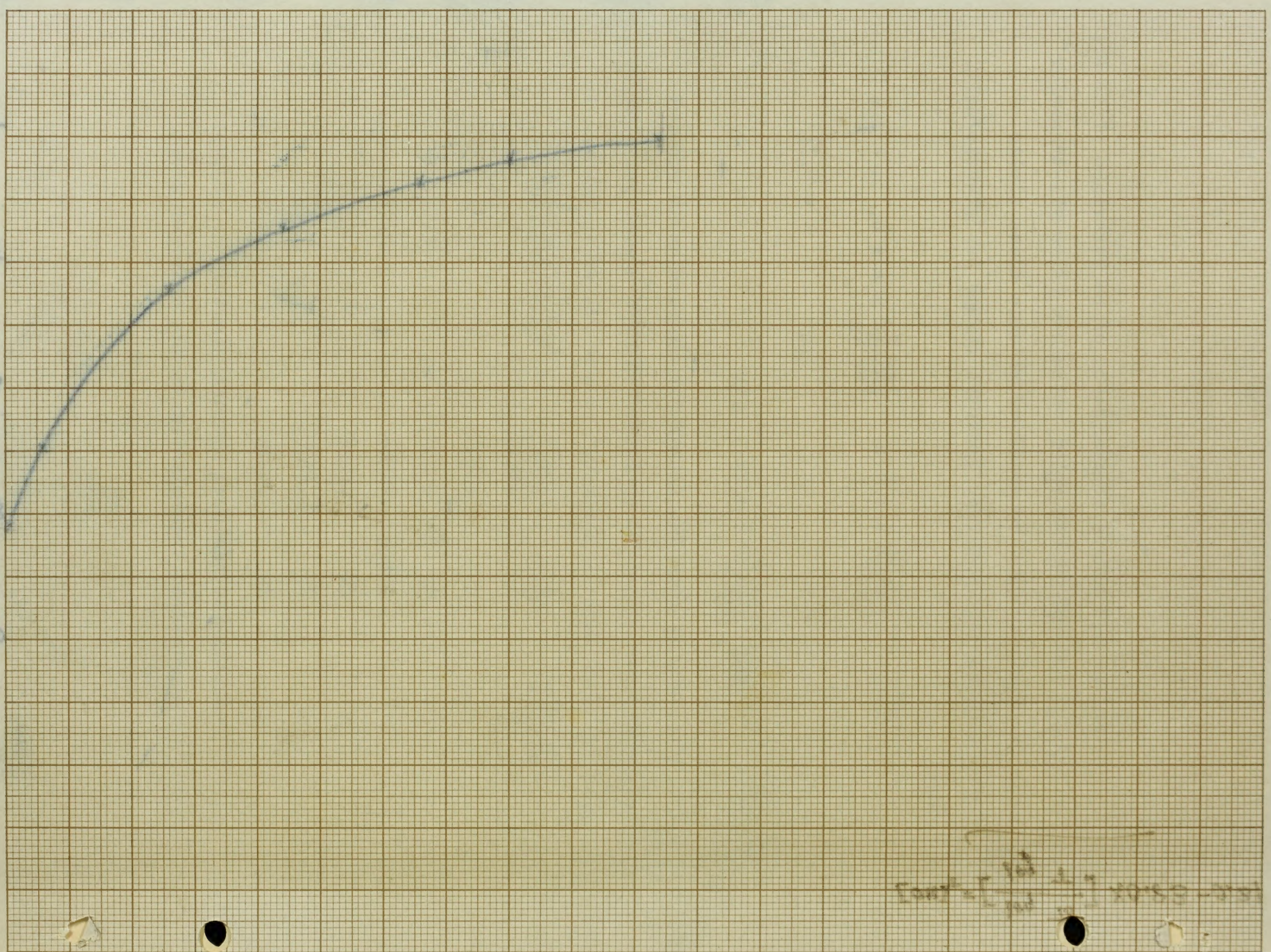


This data and the silica analyses are correlated in the following table.

Film No.	$(OH)_T$	OH replaced	Gravimetric Si/glucose	% OH* replaced
1	0.52	0	0	0
2	0.52	0	0	0
3	0.40	0.12	0.20	20.8
4	0.33	0.19	0.24	36.4
5	0.22	0.30	0.38	57.0
6	0.13	0.39	0.41	74.9
7	0.03	0.49	0.48	94.3

(Theoretically 0.52 - $(OH)_T$ = OH replaced = Si/glucose)

*-based on optical data

Discussion of Probable Reactions

The evidence presented indicates that the reactions occurring are as follows:

Mix and Film #

2 $Si(OC_2H_5)_4 \not\leftarrow$ ethyl cellulose $\longrightarrow$ no reaction

3 $Si(OC_2H_5)_4 \not\leftarrow 2H_2O \not\rightarrow = Si(OH)_2(OC_2H_5)_2$

$Si(OH)_2(OC_2H_5)_2 \not\leftarrow$ ethyl cellulose $=$ [ethyl cellulose–O–$Si(OC_2H_5)_2$]

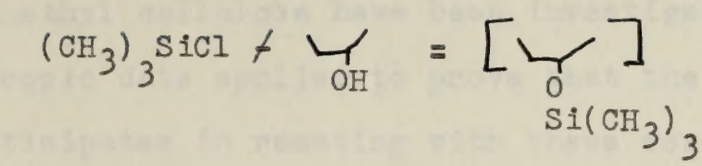
$\not\rightarrow H_2O$

4 $Si(OH)_n(OC_2H_5)_{4-n} \not\leftarrow$ ethyl cellulose $=$ [ethyl cellulose–O–$Si(OC_2H_5)_{4-n}$] $\not\rightarrow H_2O$

5 $SiCl_4 \not\leftarrow$ ethyl cellulose $=$ [ethyl cellulose–O–Si–Cl] $\not\rightarrow HCl$

6 $(CH_3)_2SiCl_2 \not\leftarrow$ ethyl cellulose $=$ [ethyl cellulose–O–$Si(CH_3)_2$] $\not\rightarrow HCl$

Mix and Film #

7 $(CH_3)_3SiCl$ + =  + HCl

Summary: the reactions of tetraethyl orthosilicate and chlorosilones with ethyl cellulose have been investigated and infra-red spectroscopic data applied to prove that the polymer hydroxyl group participates in reacting with these reagents. It is also demonstrated that tetraethyl orthosilicate does not react directly with the polymer hydroxyl group. Finally, an equation has been derived for the correlation of the 2.8 micron transmission to the residual hydroxyl content per glucose unit of the polymer.

Part 2. Reactions of Substituted Silanes with Glycols and Diamines

Introduction

Following the direction of Part 1, the object of this section is to determine the possibility of new polymer formation from the interaction of substituted polyfunctional silanes with glycols or diamines.

In the nature of condensation polymerization, the below were considered:

	Reagents			Possible Product
1.	$Si(OH)_2(OC_2H_5)_2$	+ $HOCH_2CH_2OH$	⟶	linear polymer
2.	$Si(OH)_2(OC_2H_5)_2$	+ glucose	⟶	crosslinked polymer
3.	$Si(OH)_3OC_2H_5$	+ $HOCH_2CH_2OH$	⟶	crosslinked polymer
4.	$Si(OH)_2(C_6H_5)_2$	+ $HOCH_2CH_2OH$	⟶	linear polymer
5.	$Si(CH_3)_2Cl_2$	+ $HOCH_2CH_2OH$	⟶	linear polymer
6.	$Si(C_6H_5)_2Cl_2$	+ $HOCH_2CH_2OH$	⟶	linear polymer
7.	$Si(CH_3)_2Cl_2$	+ $NH_2CH_2CH_2NH_2$	⟶	linear polymer
8.	$Si(CH_3)_2Cl_2$	+ $H_2N\text{-}CH_2CH_2NH\ CH_2CH_2NH_2$	⟶	linear and/or crosslinked polymer

Experimental

These experiments were run:

1. ten grams of dextrose in 100 cc of pyridine was refluxed with 10 cc tetraethyl orthosilicate for four hours. A soft brown gel formed.
2. as #1 using 10 grams ethylene glycol. No reaction.
3. 10 cc silicontetrachloride refluxed with 5 cc ethylene glycol to form an oil.
4. 10 grams diphenylsilicol and 10 cc of glycol refluxed to form an oil.
5. Dimethyldichlorosilanes and ethylene glycol formed an oil.
6. Diphenyldichlorosilanes and ethylene glycol formed an oil.
7. Dimethyldichlorosilanes and ethylene diamine gave a white powder.
8. Diphenyldichlorosilanes and ethylene diamine gave an oily wax.
9. Dimethyldichlorosilane and diethylene triamine gave a thermoplastic resin which became thermoset on prolonged heating.
10. 74 cc of the tetraethyl orthosilicate, 23 cc solox, 2.5 cc of water and 20 cc of ethylene glycol formed a brittle gel.

Dimethyldichlorosilanes and diphenyldichlorosilanes were prepared by the Grignard method (11).

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7. Dimethyldichlorosilanes and ethylene diamine gave a white powder.
8. Diphenyldichlorosilanes and ethylene diamine gave an oily wax.
9. Dimethyldichlorosilane and diethylene triamine gave a thermoplastic resin which became thermoset on prolonged heating.
10. 75 cc of the tetraethyl orthosilicate 25 cc water, 2.5 cc of water and 20 cc of ethylene glycol formed a brittle gel.

Dimethyldichlorosilanes and diphenyldichlorosilanes were prepared by the Grignard method(11).

Conclusions

No further analyses were carried out with reactions of silanes with glycols since these are reported by Krieble(12) to readily form cyclic structures rather than polymers due to ease of formation of strain free rings.

Reactions of polyfunctional tetraethyl orthosilicate with glycols or glucose resulted in brittle gels probably due to an excess of activity centers leading to cross linkages and short chains.

Reactions of dialkyl dichlorosilanes with diamines produce cyclic products or oils rather than polymers.

The reactions not leading to a resinous product have not been further investigated.

The primary goal of this section was attained by the resin formed in experiment #9 through the refluxing of dimethyldichlorosilane and diethylenetriamine. Refluxing for one hour produced a viscous yellow syrup which cast to a thermoplastic film. This on baking at 120°C for one hour converted to a brittle, hard, continuous yellow resin film. Silica analysis is approximately that corresponding to structure

$$\left[- NH_2CH_2CH_2NH\text{-}CH_2CH_2NH - \overset{CH_3}{\underset{CH_3}{Si}} - \right]$$

which has a residual activity center capable of further cross linking.

Summary

The object of this section was to demonstrate the possibility of polymer formation by condensation between a substituted dichlorosilane and a difunctional organic molecule such as a diamine. This resin was obtained by condensing dimethyldichlorosilane with diethylenetriamine. Further investigations are not within the scope of this thesis, but it is here suggested that similar reactions warrant extensive research in that the development of a siloxane-amine or siloxane-ethylene copolymer should produce a resin displaying physical properties intermediate to silicones and organic polymers. This is desirable since silicones require high temperatures (around 250°C) to cure fully, whereas the organic polymers soften at too low a temperature (around 120°C). The postulated new series of resins should soften at intermediate temperatures.

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